Equations of State of the Earth

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Introduction

The major results of research in the United States for 1971–1974 in the areas of static, high-pressure X ray, ultrasonic and shock wave measurements, and progress in theoretical equations of state are summarized. This 4-year period has seen the massive accumulation of new data pertinent to describing the properties, and to some extent geodynamic processes, of the upper mantle as well as exposing the gauntlet of scientific challenge with regard to our lack of detailed understanding of the major changes in crustal seismic velocities, which seem to offer so much promise for earthquake prediction. In the area of very high pressure geophysics, another challenging problem uncovered is the question of explaining the low adiabatic gradient in the outer core, which seems to be required to retain liquid iron alloy material at the melting point. Important advances in what until recently has been quite empirical elastic moduli 'systematics' have demonstrated how ionic radii and ionic packing densities may be quantitatively employed to predict unmeasured equations of state as well as tie together an ever increasing body of data for the elasticity of compounds which are crystal-chemical analogs of mantle minerals.

The lack of suitable pure and mechanically homogeneous samples has continued to offer a serious obstacle to the study of candidate materials of the earth's interior. When samples of critically important minerals have been synthesized in such laboratories as those of A. E. Ringwood and R. Liebermann (Canberra) and S. Akimoto (Tokyo), significant new experiments and, shortly thereafter, theoretical results have been forthcoming.

Several scientific meetings and meeting proceedings published in the years 1971–1974 have included contributions from the United States and have focused on the presentation of new data and theoretical interpretations. Two symposia of the International Association of Seismologists and Physics of the Earth's Interior (IASPEI) were organized at the fifteenth meeting of the IUGG: The State of Substance in the Earth's Interior (V. A. Magnitsky, Convener) and the Final Report, Upper Mantle Project (V. V. Beloussov, Chairman). Most of the papers presented at these two symposia are published in special issues of *Physics of the Earth and Planetary Interiors* (volume 5, pp. 267–343) and *Tectonophysics* (volume 13, pp. 1–644). The latter group of papers has also been published separately as a book [*Ritsema,* 1972]. The scientific reports of the Upper Mantle Project Symposium on Mechanical Properties and Processes of the Upper Mantle (Orson L. Anderson and L. R. Sykes, Conveners) held in Flagstaff, Arizona, in 1970 are published as a group in the *Journal of Geophysical Research* (volume 76(5), 1971). The proceedings of a conference held in Cambridge, Massachusetts, in April 1970 honoring Francis Birch, published in 1972 [*Robertson,* 1972], contains several articles dealing with equations of state. The proceedings of a special conference, convened by S. K. Runcorn, held at the Lunar Science Institute in March 1972, entitled Conference on High Pressure Physics and Planetary Interiors, was published in *Physics of the Earth and Planetary Interiors* (volume 6, pp. 1–209) and was also separately reprinted as a book [*Runcorn,* 1972]. At the IASPEI meeting in Lima, Peru, in August 1973, a symposium entitled The State and Behavior of Material Inside the Earth was convened by O. Anderson. Papers presented at this symposium were published individually. Numerous U.S. contributions to the NATO Institute on Petrophysics (S. K. Runcorn, Convener) held in Newcastle, U.K., on March 25–29, 1974, and the Fourth International Conference on High Pressure, on November 25–29, 1974, held in Kyoto, Japan (J. Osugi, Kyoto University, Chairman), are to be published.

A major trend in the use of the international meter kilogram second system of units has started in the United States. During the last 2 years, several laboratories largely associated with the Atomic Energy Commission, now Energy Research and Development Agency, have begun to report pressures in N/m^2, i.e., pascals. Thus 1 Mpa = 10^6 N/m^2 = 10 bars = 10^7 dyn/cm^2.

Static Pressure-Volume Measurements

New piston-cylinder, pressure-volume data for a wide class of minerals have recently been reported by Kennedy and his co-workers [*Vaidya et al.,* 1973; *Singh and Kennedy,* 1974]. Static compression data have been extended to 45 kbar for such minerals as analcite, augite, cryolite, gypsum, hedenbergite, basaltic horneblende, labradorite, talc, and wollastonite. The new high-resolution compression data for calcite [*Singh and Kennedy,* 1974] provide the first static compressibility for the high-pressure polymorph, calcite 2. This study, when it is taken with the ultrasonic measurements of *Wang* [1966, 1968] and *Wang and Meltzer* [1973] and the theoretical analysis of *Walsh* [1973*c*], provides a rather complete picture of the effect of two closely spaced, in pressure, phase changes on the elastic moduli of this material. New linear compressibility data for various water ices and ice single crystals, obtained by a novel optical cell technique, are reported to 0.31 kbar by *Gow and Williamson* [1972].

A considerable volume of new data on the behavior of elements, compounds, and minerals of geophysical interest has been produced by several laboratories using high-pressure X ray apparatus. Of general interest is a new intercomparison of metallic silver with the often used sodium chloride high-pressure X ray standard. In this study, *Liu and Bassett* [1972] mixed silver and sodium chloride and obtained new data on both silver and the high-pressure (CsCl structure) polymorph of NaCl which is stable above 300 kbar. The new data for silver, which demonstrated that it is slightly more compressible than assumed by, e.g., *Clendenen and Drickamer* [1966] in previous high-pressure X ray studies, will permit correction of these earlier data. Laser heating samples of $(Mg, Fe)_2SiO_4$ in either the olivine or ringwoodite structure, and Mg-Fe pyroxene, while under ~200 kbar causes disproportionation to magnesiowustite and stishovite. This has provided major support for the hypothesis that mixed oxides may represent the high-pressure assemblage of the lower mantle [e.g., *Ming and Bassett*, 1974]. Thus the study of the compressions of oxides has taken on special geophysical importance. New data for SrO (NaCl structure) [*Liu and Bassett*, 1973] to 340 kbar indicate the occurrence of a tetragonal distortion between 70 and 307 kbar. Study of the compression of BaO (NaCl structure) to 290 kbar has revealed the occurrence of two new phases. BaO(II) has a tetragonal structure which occurs above 92 ± 3 kbar and is ~5% denser than BaO(I); BaO(III) at 140 ± 5 kbar is 7% denser than BaO(II) and has a tetragonal PH_4I structure. Liu and Bassett suggest that if MgO undergoes a high-pressure phase change, these two high-pressure phases may be analog candidate structures.

Measurements on magnetite to 320 kbar by *Mao et al.* [1974] provide a new value of bulk modulus of 1.83 ± 0.10 kbar, which is higher than many of the scattered data available previously. A new phase with monoclinic symmetry is observed above 250 kbar. The phase change appears reversible. The density of the high-pressure phase is 2% greater than magnetite at the transition pressure and appears consistent with a structure in which all the iron is octahedrally coordinated.

If the lower mantle of the earth has significant quantities of mixed oxides, detailed knowledge of the equation of state of stishovite is critical to the interpretation of the seismic data [e.g., *Davies*, 1974]. *Liu et al.* [1973*a*] have provided new high-pressure X ray data to 223 kbar for this mineral. Their fit to the new data gives a value of 3.35 Mbar for the isothermal bulk modulus, which is comparable to values obtained by ultrasonic and shock wave techniques. Important for a complete description of the thermal equation of state, thermal expansion data for stishovite have been obtained by *Weaver* [1971]. Additional compression data to 280 kbar for Co_2SiO_4, which is isostructural with ringwoodite, (Mg, Fe)SiO_4, which is believed to exist in the mantle between a depth of 350 and 650 km, are reported by *Liu et al.* [1973*b*]. The bulk modulus, 2.10 ± 0.06 Mbar, is similar to other spinels. In the same paper, data for the compression of magnesian ilmenite (bulk modulus, 1.68 ± 0.14 Mbar) are reported for the first time. This mineral is isostructural with a proposed high-pressure polymorph of pyroxene. Additional data for a Mg-rich garnet to 100 kbar which agree with both X ray and ultrasonic results are reported by *Duba and Olinger* [1972]. The compression of a calcium-rich garnet has also been studied by *Halleck* [1973]. In 1971, *Olinger and Duba* [1971] reported high-pressure X ray data which indicated that to pressures of ~100 kbar, the density of olivine was ~1% lower than that inferred from the ultrasonic data [*Graham and Barsch*, 1969] extrapolated via finite strain theory, the shock wave data of *McQueen et al.* [1967] and *Ahrens et al.* [1971], and *Bridgman*'s [1948] 40-kbar compression data. These data were obtained in a Jamieson-type apparatus. Subsequent work by *Schock et al.* [1972] using a Bassett-Takahashi type apparatus supported the discrepant observation of Olinger and Duba, and the more compressible ultrasonic result was tentatively ascribed to possible defects detected by the ultrasonic waves. In a later paper [*Olinger and Halleck*, 1974] this discrepancy has apparently been resolved, and the most recent X ray data now agree with the extrapolation to 100 kbar of *Graham and Barsch*'s [1969] 10-kbar ultrasonic results.

Of interest to physical oceanographers are the syntheses of sound speed measurements of water and seawaters of various salinities into complete *P-V-T* equations of state reported by *Wang and Millero* [1973]. The range of their parameterization of the water equation of state is 0°–90°C and 0–1 kbar.

Ultrasonic Equations of State

Since 1971 a considerable quantity of high-precision ultrasonic data for single crystals or nearly pore-free polycrystalline samples of olivine, pyroxene, and garnet, the likely minerals of the upper mantle, have been reported as a function of temperature and pressure. *Chung* [1971] reported zero pressure data and temperature and pressure derivatives for a suite of artificial hot-pressed olivine aggregates of compositions Mg_2SiO_4, $(Mg_{0.95}, Fe_{0.05})_2SiO_4$, $(Mg_{0.90}, Fe_{0.10})_2SiO_4$, $(Mg_{0.85}, Fe_{0.15})_2SiO_4$, $(Mg_{0.80}, Fe_{0.20})_2SiO_4$, $(M_{0.50}, Fe_{50})_2SiO_4$, and Fe_2SiO_4. For olivine near-pure forsterite compositions, Chung's bulk and shear moduli are slightly lower than the previous single-crystal data of *Kumazawa and Anderson* [1969] and *Graham and Barsch* [1969]. For a fayalite composition the bulk modulus, 1.22 Mbar, is considerably greater than previous data on less pure samples. Precision elastic constant data for a pyroxene, bronzite, as a function of pressure and temperature, are reported for the first time by *Frisillo and Barsch* [1972]. Of special interest is the reported high value of $(\partial K_s/\partial P)_T$ of 9.6, which is twice that of other candidate mantle minerals. *Frisillo and Baljan* [1972] have also reported data on thermal expansivity of single-crystal bronzite to 1000°C. Additional elasticity data as a function of pressure have been reported for spessartite almandine [*Wang and Simmons*, 1974] and grossular garnet [*Halleck*, 1973]. New data for the elasticity of stoichiometric spinel as a function of pressure to 10 kbar are reported by *Chang and Barsch* [1973]. The new data for the effect of pressure on the elastic moduli are in good agreement with the earlier data of *Schreiber* [1967] for a non-stoichiometric spinel. Moreover, these authors found a value of the second derivative of the adiabatic bulk modulus which was about 10 times greater than that observed previously for alkali halides. This result implies both a markedly nonlinear behavior with pressure of compressional wave velocity and a density above ~80 kbar. New elasticity data for the spinel, $Mg_{0.75}Fe_{0.36}Al_{1.9}O_4$ (pleonaste), are reported to a pressure of 5 kbar, for certain modes, they are reported to 100°C, and for $FeAl_2O_4$ (hercynite) they are reported at room temperature by *Wang and Simmons* [1972*a*]. As in other spinel compositions the pressure derivatives of shear moduli are slightly negative.

Because of continued interest in interpreting the seismic properties of the lower mantle in terms of equivalent oxides, continued work on elastic properties has been reported. New data on the elastic properties of sintered polycrystalline NiO obtained via conventional ultrasonic pulse transmission resonant sphere and composite oscillator techniques are given by *Notis et al.* [1971].

The first compressional and shear ultrasonic data on a 1-mm-long 1.5-mm-diameter sample of synthetic polycrystalline stishovite are reported by *Mizutani et al.* [1972]. The elasticity of a single crystal of a crystal-chemical analog of stishovite, GeO_2, and its pressure derivatives is reported by *Wang and Simmons* [1973]. Other analog studies of the elasticity of germanates have been carried out for GeO_2 (quartz and stishovite structure) and Mg_2GeO_4 (olivine) by *Soga* [1971]. An empirical relation for the compressional and shear velocity in terms of density and mean atomic weight similar to several others recently proposed (discussed below) is also given. Other measurements of the elasticity of oxides include the study of

Son and Bartels [1972] of the properties of single-crystal CaO and SrO under hydrostatic pressure. Of possible importance with regard to the effect of domain-wall-stress interaction on elastic constant measurements of transition element–bearing oxides and silicates is the study of *Liebermann and Banerjee* [1971], who report data on the moduli of hematite as a function of magnetic field and temperature.

The results of *Shaw* [1974], who measured the elastic constants of a series of polycrystalline samples of alkali halides (AgI, NH_4I, RbCl, RbBr, RbI) both below and above major pressure-induced phase changes taking place in the pressure interval below 10 kbar, are important with regard to evaluating phase changes in the earth. He points out that in general the percentage change due to polymorphic transition in shear velocity is considerably greater than that in compressional velocity, a feature seen in several seismic models for the transition region of the mantle.

The effect of hydrostatic pressure on the intrinsic elasticity properties of rocks, above the pressure regime where crack closing effects predominate, has finally been determined. Both *Christensen* [1974] and *Wang* [1974] report travel time compressional ultrasonic velocity data to 30 and 25 kbar for candidate upper mantle rocks. These new data are obtained by using the Bridgman-Birch 30-kbar apparatus and an organic fluid pressure medium. In the case of Christensen's data the pressure derivative of compressional velocity for dunites agrees with the single-crystal results, both his and Wang's results for bronzitite giving a markedly lower pressure derivative than that obtained by *Frisillo and Barsch* [1972]. *Manghnani et al.* [1974] have reported the compressional and shear velocities of 22 granulite and eclogite facies rocks to 10 kbar and applied the results to examining the mean atomic weight of the lower crust and upper mantle in several regions. *Kumazawa and Helmstaedt* [1971] have similarly examined the elastic velocities in a series of eclogite xenoliths from kimberlites and found that they display considerably less anisotropy than was observed in dunites and peridotites. *Christensen* [1973] has measured the *P* and *S* wave velocities in monomineralic rocks composed of $MgCO_3$, $FeCO_3$, and $MnCO_3$ to 10 kbar and found that the velocity systematics is similar to that observed in the olivine series.

With the availability of good single-crystal elastic constant data for minerals such as olivine and pyroxene and the measurement of both elastic constants and crystal orientation as a function of direction in such important mantle rock types as dunite, it has been possible to test elastic constant averaging theories for rocks. *Crosson and Liu* [1971], *Christensen and Ramananantoandro* [1971], and *Babuska* [1972] have carried out such studies. Although their conclusions differ somewhat, all three groups find that at high pressures the anisotropy in dunite is closely correlated with preferred orientation of crystals rather than crack geometry. *Peselnick et al.* [1974] have carried out a similar study for oriented lherzolite samples from the Lanzo massif and found that the anisotropy observed in core samples correlated with that inferred from regional geophysical studies. *Birch* [1972] has pointed out that laboratory experiments on coarse-grained samples with short-wavelength signals provide upper limits to the velocities measured seismologically and has shown how the systematically averaged crystal velocity data are, in general, different from the bulk properties of the single crystal. *Walsh* [1973*a*] has examined this problem from a thermodynamic viewpoint and has pointed out that the small differences related to thermal equilibrium between different oriented crystallites within a rock can give rise to a small compressibility dependence on frequency in an aggregate. *Spetzler et al.* [1972] have examined the effect of internal stresses on the measurements of the pressure derivative of the bulk modulus; they found that the measured value will be too low if residual pores are filled with the pressurizing medium and are connected. *Fancher and Spetzler* [1973] have suggested a modification to Kroner's averaging theory which takes into account a correction related to the directionally dependent Young's modulus for predicting the response of a hot-pressed aggregate to temperature and pressure variation. *Walsh* [1973*b*] has examined this problem and the theoretical thermal expansion and specific heat for an aggregate by using a general thermodynamic approach. His theory predicts the thermal and pressure states for hot pressing which will minimize internal strains of the resulting aggregate.

Observations of the effect of ultrasonic waves interacting with a rock (limestone) in which the major mineral (calcite) is undergoing a polymorphic phase change (calcite 1–calcite 2 and calcite 2–calcite 3) by *Wang and Meltzer* [1973] indicate that the characteristic reaction time of the first of these transitions is $\sim 0.05\ \mu s$ and is associated with a marked increase in attenuation and decrease in velocity. In the same issue of the *Journal of Geophysical Research, Walsh* [1973*c*] provides a theoretical model of the interaction of seismic waves and rocks undergoing polymorphic transition which predicts that V_p/V_s will have low values for this situation relative to high values for V_p/V_s for the situation where enhancement of attenuation results from partial melting.

Tilmann and Bennett [1973] have carried out some exploratory ultrasonic shear wave birefringence experiments on a wide variety of rocks and demonstrated that at least in centimeter-sized samples this effect is pronounced in many rock types. *Todd et al.* [1973] have described several sources of acoustic birefringence as a result of mineral and crack orientation in indurated rocks. *Bennett* [1972] has further attempted to demonstrate that an elastic stiffness ellipsoid, measured ultrasonically, provides a technique for orientation of single crystals, as well as generally permits the quantitative description of the elastic anisotropy of a rock. On the former point, his conclusions [*Bennett,* 1974*a, b*] have been strongly challenged by *Dandekar and Fowles* [1974*a, b*].

The effect on seismic velocity and attenuation of variable viscosity fluids in narrow pore openings in rock has been described by *Nur* [1971] with regard to the expected properties of a partially molten upper mantle low-velocity zone. New experimental data on the effect on ultrasonic *P* and *S* velocities in water-saturated rocks of lowering the temperature below the water-ice (1) transition point and on an anomaly in the behavior of the rock shear modulus are reported by *Takeuchi and Simmons* [1973]. A theoretical study by *O'Connell and Budiansky* [1974] has provided a framework by which thin section analysis of crack trace density and mean length can be convolved with effective bulk rock properties to provide predictions of seismic velocities as a function of fluid saturation.

The suggestion of *Gupta* [1973] that shear wave birefringence on a large scale might provide a premonitory effect prior to an earthquake has provided some motivation to examine this phenomenon both experimentally and theoretically. Recently, *Bonner* [1974] has demonstrated the effect of shear wave birefringence ($\sim$11% magnitude) during dilatant deformation of granite under hydrostatic confinements of ~200 bars. *Anderson et al.* [1974] have shown that fluid-filled elliptical cracks give rise to an appreciable anisotropy for both *P* and *S* waves and have shown how the ratio V_p/V_s is expected to vary with direction during dilatancy. The relationship between the effect of stress-induced crack closure under hydrostatic conditions and the seismic velocity under uniaxial stress in different directions is derived by *Nur* [1971]. Several studies of ultrasonic velocities and attenuation in dry granular media have been motivated by concomitant measurements on lunar samples. *Jones* [1973] has reported the dependence of longitudinal velocity and attenuation in various composition and grain size powders. *Pilbeam and Vaišnys* [1973] have demonstrated how attenuation in aggregates can under moderate pressure reach the low values inferred on the moon via contact theory. *Talwani et al.* [1973] and *Warren and Anderson* [1973] report an extensive series of measurements of elastic properties of various terrestrial granular media under pressure. *Warren* [1973] demonstrated how thermal pulses can, by presumably removing grain-grain contact volatile constituents, radically increase the *Q* of rock powders.

Of interest to marine geophysicists is *Hamilton*'s [1971] extensive series of measurements of density and elastic velocities which are reported for a variety of unconsolidated oceanic sediments. The effect of dissolved CO_2 on the sound velocity of seawater is reported by *Hulsemann* [1972].

Shock Wave Equations of State

The question of the composition and thermal state of the core of the earth is inevitably intertwined with the correlation of seismic models, studies of the thermal regime, and high-pressure and high-temperature shock wave and theoretical equations of state for metals. Considerable motivation for research has come from a series of papers [*Higgins and Kennedy*, 1971; *Kennedy and Higgins*, 1973*a*, *b*] in which it has been pointed out that from a simple extrapolation of melting relations for iron and the assumption that the outer core temperatures coincide with the local melting point and no internal heat sources and sinks are present, it follows that the adiabatic gradient is less than the melting point gradient. Hence the core rather than convecting is stably stratified! Although reanalysis of the shock wave data for iron [*Stewart*, 1973] still indicates (8–20%) Si-bearing iron core, exceptions to the assumptions of Higgins and Kennedy have been expressed by *Busse* [1972], who has suggested that convection takes place in a two-phase solid-liquid system in the core. *Verhoogen* [1973] in part on the basis of *Leppaluoto*'s [1972] calculation of the iron melting point of 7000°K at the inner core-outer core interface (versus 5000°K from Higgins and Kennedy) proposes an iron sulphide core similar in composition to that proposed earlier for the earth by *Murthy and Hall* [1972] and *Anderson et al.* [1971] and also for Mars [*D. L. Anderson*, 1972]. A sulfur content of 10–15 wt % for the outer core was inferred on the basis of shock wave data for iron sulphide by *King and Ahrens* [1973]. *Barker and Hollenbach* [1974] have carried out a detailed study of the $\alpha \rightleftarrows \epsilon$ phase change in iron and discovered that although the $\alpha \rightarrow \epsilon$ transition occurs at 130 kbar, the reverse, $\epsilon \rightarrow \alpha$ transition, occurs at only 98 kbar. This result possibly implies that the equilibrium pressure of this phase change is ~114 kbar, rather than the 130-kbar value previously inferred.

New shock wave Hugoniot data for silicates are reported for bronzite [*Ahrens and Gaffney*, 1971], forsterite [*Ahrens et al.*, 1971], orthoclase [*Ahrens and Liu*, 1973], and almandine garnet [*Graham and Ahrens*, 1973]. Since these and virtually all previous studies have demonstrated the occurrence of various shock-induced high-pressure phases presumably corresponding to lower mantle phases, the interpretation of these data in terms of high-pressure mineralogy continues to be of interest. With the exceptions of quartz [*Kleeman and Ahrens*, 1973] and garnet [*Ahrens and Graham*, 1972], virtually all silicates yield glasses [e.g., *Kleeman*, 1971] or the deformed starting phase upon shock recovery in the laboratory. *Davies and Anderson* [1971] have utilized increased knowledge of equation of state systematics to revise estimates of the equations of state derived from shock wave data. Both *Davies* [1972] and *Graham* [1973] carried out detailed studies of the equation of state of stishovite (and also a coesitelike phase in the case of Davies) largely because of the importance of this mineral to the study of the lower mantle. *Grady et al.* [1974] have demonstrated via release adiabat measurements on quartz, shocked to states in the 150- to 400-kbar regime, that the high-pressure shocked material unloads along a path characteristic of a quartz-stishovite mixture. *Anderson* [1974] has examined the volume dependence of Gruneisen ratio (γ) on the basis of thermodynamics for various oxides and silicates and finds the marked dependence of γ with compression for the stishovite structure inferred by others on the basis of shock wave data consistent with ultrasonic and thermodynamic data. *Davies and Gaffney* [1973] have employed crystal-chemical relations to estimate densities and, in turn, equation of state systematics to predict Hugoniots corresponding to various high-pressure phases.

In the case of geophysically important minerals such as MgO and Al_2O_3 which do not undergo phase changes over the available pressure range, shock wave data have been the traditional testing ground for finite strain equations of state. *Davies* [1973] has provided a generalization of fourth-order finite strain theory, while *Ahrens and Thomsen* [1972] have compared the predictions of the Lagrangian and Eulerian formulations of finite strain theory to shock wave data for a wide variety of solids.

Because of the necessity of extrapolating the usual low-pressure ultrasonic data to high pressure in geophysics, it is important to test finite strain theories which predict the effect of a large compression on the shear properties [e.g., *Davies*, 1974]. Since bulk properties are obtained from the usual Hugoniot experiments, some data on shear modulus can be obtained from high-pressure data for the longitudinal wave velocity [*Anderson*, 1974]. Some initial data for MgO longitudinal wave velocity to 528 kbar are reported by *Davies and Ahrens* [1973].

A new explosive-driven isentropic magnetic compression technique has been applied to fused quartz and liquid hydrogen by *Hawke et al.* [1972]. At 5 Mbar an approximate volume of 0.15 cm^3/g is obtained for fused quartz, at which point it remains nonconducting. *Gaffney and Ahrens* [1973] have described a new shock technique for obtaining the absorption spectra of minerals under shock compression to very high pressures.

The strength and stress differences present in sapphire and granite under dynamic loading are investigated by *Graham* [1971] and *Schock and Heard* [1974], respectively. A detailed comparison of uniaxial loading under quasi-static and shock loading is reported by *Brace and Jones* [1971]. Numerical methods which can be used to invert particle velocity and pressure profiles from a spherically propagating stress wave in rock to obtain constitutive relations between density, pressure, and deviatoric stress are presented by *Grady* [1973].

Pursuant to describing intense stress wave propagation from underground explosions, *Butkovich* [1971] has described the effect of vaporization of water contained in surface rocks on this process, while *Garg* [1971] and *Morland* [1972] have described constitutive relations for generalized fluid-rock systems. Recently, *Morland* [1974] has also developed a theoretical framework for modelling stress wave propagation in jointed rocks.

Theoretical Equations of State

New understanding, in terms of lattice dynamics, of the experimental data derived from ultrasonic and static compression data for minerals has come as a result of two important papers by *Shankland* [1972] and *Chung* [1972] in which, independently, the relationship of the slopes of compressional, bulk, or shear velocity versus the density plots of *Birch* [1961] is related to the Gruneisen ratio of each particular vibrational mode. A second concept brought out in both papers is an understanding of how the variation of velocity with density, for a particular crystal structure, depends on the relationship between molar volume and mean atomic weight for the structure. Important precursors to these papers are embodied in the ideas presented by *Anderson* [1967] and *O. L. Anderson* [1972*a*, *b*], both dealing with systematics of equation of state parameters. *Chung* [1974] adds new data to the above relationships for Mg_2GeO_4, Fe_2GeO_4, and Fe_2SiO_4 (both in the olivine and spinel structures) and GeO_2, SnO_2, and SiO_2 in the rutile structure. *Soga*'s [1971] paper reports a velocity-density relationship for this isomorphous series similar to the relationships of Chung. A further generalization of their two independent papers, specifying the dependence of the bulk sound speed on ionic radii, is given in the work by *Shankland and Chung* [1974]. On the basis of Birch's law, *Chung* [1972] demonstrated that the prediction of the elastic moduli for the spinel phases of $(Mg, Fe)_2SiO_4$ agreed with the pressure-volume data for these spinels measured by *Mao et al.* [1969]. Similar predictions of the equations of state of other high-pressure phases, of interest to study of the lower mantle, are presented in the work by *Chung* [1973]. *Davies* [1974] has proposed a novel scheme for examining the elastic properties of A_2BO_4 (olivine stoichiometry) and ABO_3 (pyroxene stoichiometry) minerals normalized with respect to the properties of a hypothetical mixture of dense oxides.

Anderson [1973] has proposed a scaling relationship for predicting the pressure derivative of the bulk modulus (K_0') for a series of similar mean atomic weight minerals based on finite strain theory, given a single experimental value for one of the series. Both *Spetzler and Anderson* [1971] and *Mao* [1974] have discussed the problems of calculating K_0 and K_0' from redundant ultrasonic data and pointed out several difficulties and inconsistencies in the data for single and polycrystalline MgO.

Thomsen [1972*a*, *b*] has discussed the application of *Kroner*'s [1967] theory for calculating the elastic constants of polycrystals from single-crystal data to the problems of calculating properties of mineral aggregates at normal and elevated pressures.

Weidner and Simmons [1972] have proposed a semiempirical interatomic force model for a wide range of alkali halides and for quartz. *Anderson and Demarest* [1971] and *Demarest* [1972] have taken Born-Mayer and Lennard-Jones (anion-anion repulsion) potentials and fit these to elastic moduli to predict the pressure for lattice instability and thus upper pressure bounds for phase transitions. *Thomsen* [1971] has examined lattice instability by applying his fourth-order finite elastic equation of state. *Demarest* [1972*a*] has also reported the results of calculation of the Gruneisen parameter (γ) over the entire vibrational spectrum for alkali halides and predicts the variation of γ with density for an assumed centrosymmetric potential function. *Knopoff and Shapiro* [1972] have reviewed theories of melting and the Gruneisen parameter of liquid metals.

Equations of State of the Mantle

Detailed mineralogic models of the upper mantle based on equations of state, taking into account equilibrium distribution of major elements between minerals, are given by *Ahrens* [1972*a*, *b*, 1973]. Melting temperatures for the whole mantle, based on estimates of equations of state, and systematics of melting relations are derived by *Kennedy and Higgins* [1972]. Based on reduction of shock wave data and crystal-chemical systematics of ionic radii, *Gaffney and Anderson* [1973] have explored the consequences of a series of presumed lower mantle transitions of silicates in which Fe^{2+} is in the low-spin electronic orbital configuration in various silicate phases. *Liu* [1973] has examined bulk sound velocity-density relations and seismic results and shown that there is a trade-off of increasing the FeO or SiO_2 content of the lower mantle relative to the upper mantle, so as to satisfy all the data. A similar conclusion was reached by *Davies* [1974*c*], who also examined the effect of the unknown temperature profile. *Wang and Simmons* [1972*b*] have also pointed out that simple averaging schemes for molar volumes lead to inconsistent inferred mantle compositions in contrast to the conclusions of *Anderson et al.* [1971]. *Mao* [1974], taking into account a dependence on Poisson's ratio in *Shankland and Chung*'s [1974] systematics, finds that the seismic data for the whole mantle can be reconciled with a nearly constant mean atomic weight.

Liu [1974] has pointed out some previously overlooked features present in the sound velocity versus density systematics of Birch for a full range of elements in the periodic table. He demonstrates that such high *Z* elements as Rb and Sr and Ge, Zr, and Ba are compatible with the densities of the mantle and core, respectively.

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